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(71)(72) Applicants and Inventors: DOLPHIN, David, H. [CA/CA]; 4464 West 12th Avenue, Vancouver, British Columbia V6R 2R2 (CA). NAKANO, Taku [JP/JP]; 950, Sata, Tamaki-cho, Watarai-gun, Mie-ken 519-04 (JP). KIRK, Thomas, Kent [US/US]; 7814 Oxtrail Way, Verona, WI 53593 (US). MAIONE, Theodore, E. [US/US]; 153 Thoreau Street, Apt. 2, Concord, MA 01742 (US). FARRELL, Roberta, L. [US/US]; 177 Hobart Street, Danvers, MA 01923 (US). WIJESEKERA, Tilak, Panini [LK/CA]; 2902 E. 54th Avenue, Vancouver, British Columbia V5S 1Y5 (CA).

(74) Agent: VILA, Richard, E.; Patent Department, Sandoz Corporation, 59 Route 10, East Hanover, NJ 07936 (US).

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(54) Title: PORPHYRINS, THEIR SYNTHESES AND USES THEREOF

(57) Abstract

Disclosed are tetraphenyl porphyrins which are beta-substituted by fluoro or chloro and/or bear electronegative substituents on the phenyl including one or two water solubilizing substituents. The new porphorins are particularly suitable as catalysts in a variety of oxidative reactions and methods.

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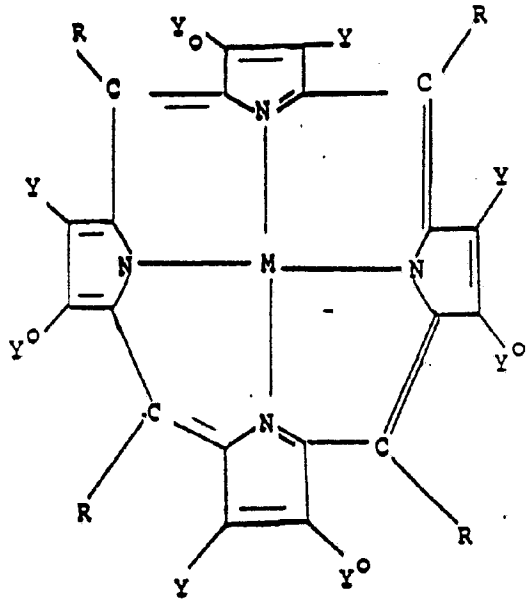
AMNEDED CLAIMS

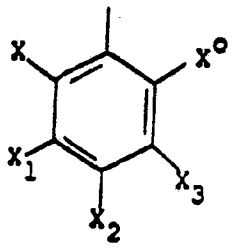
[received by the International Bureau on 30 September 1988 (30.09.88)
original claims 1-5, 9-13, 17-28, 31-33, 37 and 38 amended; new claims 39 and 40 added;
other claims unchanged (7 pages)]

1. A compound of the formula:



I

wherein M is a transition metal capable of sustaining oxidation, said M being optionally axially ligated to a ligand, each Y and Y^o on each 5-membered ring is independently H, fluoro or chlori, each R ring is



X and X^o are independently H or a non-water solubilizing electronegative group, and X_1, X_2 and X_3 are independently H or an electronegative group, subject to the provisos that:

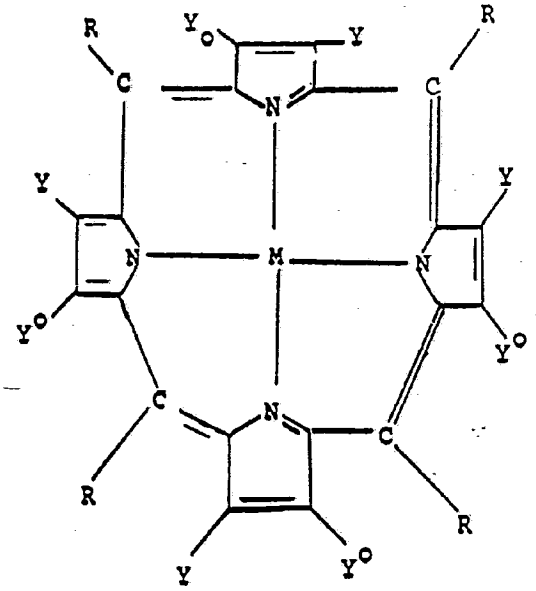
1) when none of X_1, X_2 and X_3 is in a water solubilizing group, then at least one of Y and Y^o on each 5-membered ring is other than H,

2) when Y and Y^o are both H, at least one but not more than two of X_1, X_2 and X_3 is a water solubilizing group and at least two of X, X^o, X_1, X_2 and X_3 is a non-water solubilizing electronegative group, or the water soluble salts thereof in which said water solubilizing groups are in corresponding water soluble salt form, and

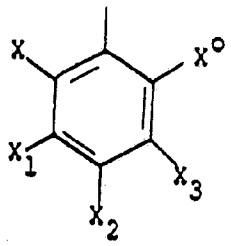
3) no more than two of X_1, X_2 and X_3 is a water solubilizing group,

or a compound of the formula I in which the water solubilizing groups are in water soluble salt form.

2. A compound of claim 1 of the formula:



wherein M is a transition metal capable of sustaining oxidation, said M optionally axially ligated to a ligand, each Y and Y^o on each 5-membered ring is independently H, fluoro or chloro, each R ring is



X and X^o are independently H, fluoro, chloro, bromo or NO_2, X_1, X_2 and X_3 are independently, H, fluoro, chloro, bromo, SO_3H, COOH or NO_2, subject to the provisos that

1) when none of X_1, X_2 and X_3 is SO_3H or COOH, then at least one Y and Y^o on each 5-membered ring is other than H,

2) when Y and Y^o are both H, at least one but not more than two of X_1, X_2 and X_3 is SO_3H or COOH, and at least two of X and X^o and the X_1, X_2 and X_3 which are not SO_3H or COOH or NO_2 are independently fluoro, chloro, bromo or NO_2, and

3) no more than two of X_1, X_2 and X_3 are SO_3H or COOH,

or a compound of the formula I in which SO_3H and COOH groups are in water soluble salt form.

3. A compound of claim 2 in which at least one Y and Y^o on each 5-membered ring is fluoro or chloro.

4. A compound of claim 3 in which both Y and Y^o on each 5-membered ring are independently fluoro or chloro.

5. A compound of claim 3 in which both Y and Y^o on each 5-membered ring are chloro.

6. A compound of claim 3 in which at least two of X, X^o, X_1, X_2 and X_3 is fluoro, chloro or bromo.

7. A compound of claim 5 in which at least two of X, X^o, X_1, X_2 and X_3 are fluoro, chloro or bromo.

8. A compound of claim 6 in which at least two of X, X^o, X_1, X_2 and X_3 are chloro.

9. The compound of claim 7 in which at least two of X, X^o, X_1, X_2 and X_3 are chloro.

10. The compound of claim 5 in which each of X, X^o, X_1, X_2 and X_3 are H and M is Fe.

11. The compound of claim 9 in which X and X^o are each chloro, X_1, X_2 and X_3 are each H and M is Fe.

12. The compound of claim 11 in chloride axially ligated form.

13. The compound of claim 9 in which X, X^o, X_1, X_2 and X_3 are each chloro and M is Fe.

14. A compound of claim 2 in which at least one but not more than two of X_1, X_2 and X_3 is SO_3H or COOH and at least two of X, X^o, X_1, X_2 and X_3 are independently fluoro, chloro or bromo, or a salt form thereof.

15. A compound of claim 14 in which one of X_1, X_2 and X_3 is SO_3H or COOH and at least two of X, X^o, X_1, X_2 and X_3 are fluoro or chloro, or a salt form thereof.

16. A compound of claim 15 in which one of X_1, X_2 and X_3 is SO_3H or a salt form thereof.

17. Compound of claim 16 in which Y and Y^o on each 5-membered ring are independently fluoro or chloro.

18. The compound of claim 16 in which Y and Y^o are each H on each 5-membered ring, X and X^o are each chloro, X_1 is SO_3H, X_2 and X_3 are each H and M is Fe, or a salt form thereof.

19. The compound of claim 18 in chloride axially ligated form.

20. The compound of claim 17 in which Y and Y^o are chloro on each 5-membered ring, X and X^o are each chloro, X_1 is SO_3H, X_2 and X_3 are each H and M is Fe, or a salt thereof.

21. The compound of claim 5 in which X, X^o, X_1 and X_3 are H, X_2 is SO_3H and M is Fe, or a salt form thereof.

22. A compound of claim 14 in which Y and Y^o on each 5-membered ring are chloro.

23. The method of modifying or degrading lignin in wood comprising treating the wood with a lignin modifying or degrading effective amount of a compound of claim 1.

24. The method of modifying or degrading lignin in wood comprising treating the wood with a lignin modifying or degrading effective amount of an oxidant in the presence of a catalytic effective amount of a compound of claim 2.

25. The method of modifying or degrading lignin in wood or pulp comprising treating the wood or pulp with a lignin modifying or degrading effective amount of an oxidant in the presence of a catalytic effective amount of a compound of claim 3.

26. The method of claim 24 in which the wood is in the form of wood chips.

27. The method of claim 25 in which the wood is thermal mechanical pulp.

28. The method of claim 26 in which kraft pulp is bleached.

29. In the method of hydroxylating an alkane or cycloalkane by oxidation in the presence of a catalytic effective amount of a porphyrin, the improvement comprising employing therein as the porphyrin a compound of claim 1.

30. In the method of epoxidizing an alkene or cycloalkene by oxidation in the presence of a porphyrin, the improvement comprising employing therein as the porphyrin a compound of claim 1.

31. The method of claim 29 in which the hydroxylation is carried out in an inert organic solvent in which the porphyrin is dissolved.

32. The method of claim 30 in which the epoxidation is carried out in an inert organic solvent in which the porphyrin is dissolved.

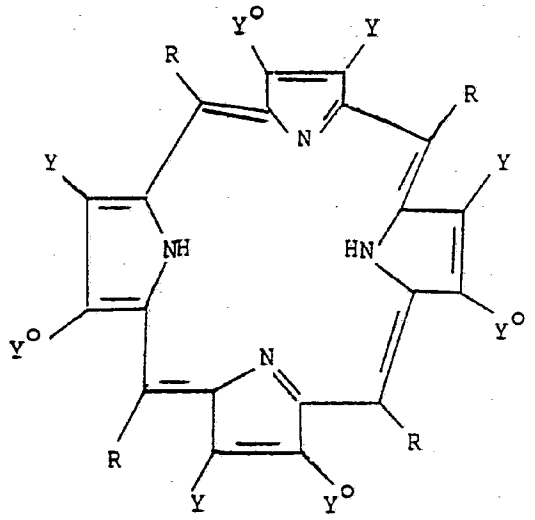
33. The compound of claim 1 in which no more than one of X_1, X_2 and X_3 is a water solubilizing group.

34. A compound of claim 1 in which Y and Y^o are H, X and X^o are chloro, X_1 and X_2 are H and X_3 is an electronegative group.

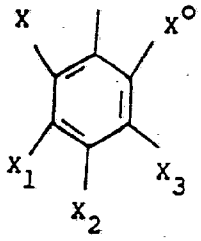
35. A compound of claim 34 in which X_3 is a water solubilizing group, or a water soluble salt form thereof.

36. A compound of claim 35 in which X_3 is a water solubilizing group in free acid form.

37. Compound of the formula



wherein each Y or Y^o on each 5-membered ring is independently H, fluoro or chloro, each R ring is



X and X^o are independently H or a non-water solubilizing electronegative group, and X_1, X_2 and X_3 are independently H or an electronegative group, subject to the provisos that:

1) when none of X_1, X_2 and X_3 is in a water solubilizing group, then at least one of Y and Y^o on each 5-membered ring is other than H;

2) when Y and Y^o are both H, at least one but not more than two of X_1, X_2, and X_3 is a water solubilizing group and at least two of X, X^o, X_1, X_2 and X_3 is a water-solubilizing electronegative group or the water soluble salts thereof in which said water solubilizing groups are in corresponding water soluble salt form; and

3) no more than two of X_1, X_2 and X_3 is a water solubilizing group,

or a compound of the formula I in which the water solubilizing groups are in water soluble salt form.

38. A compound according to claim 35 wherein at least one of Y and Y^o on each 5-membered ring is other than H.

39. A method of treating a waste stream containing chlorinated organic contaminants comprising treating the waste stream with a degrading effective amount of an oxidant in the presence of a catalytic effective amount of a compound of claim 1.

40. A method of claim 39 in which the waste stream is E1 effluent.